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Reducing Logistics Footprints and Replenishment Demands: Nano-engineered Silica Aerogels a Proven Method for Water Treatment

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Executive Summary

Rapid deployment and the use of objective force aggressively reduce logistic footprints and replenishment demands. Maneuver Sustainment requires that Future Combat Systems be equipped with water systems that are lightweight, have small footprints, and are highly adaptable to a variety of environments. Technologies employed in these settings must be able to meet these demands.

Lawrence Livermore National Laboratory has designed and previously field tested nano-engineered materials for the treatment of water. These materials have been either based on silica aerogel materials or consist of composites of these aerogels with granular activated carbon (GAC). Recent tests have proven successful for the removal of contaminants including uranium, hexavalent chromium, and arsenic. Silica aerogels were evaluated for their ability to purify water that had been spiked with the nerve agent VX (O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate). These results demonstrated that silica aerogels were able to remove the VX from the supply water and were nearly 30 times more adsorbent than GAC. This performance could result in REDUCING CHANGEOUT FREQUENCY BY A FACTOR OF 30 or DECREASING the VOLUME of adsorbent BY A FACTOR OF 30; thereby significantly reducing logistic footprints and replenishment demands. The use of the nano-engineered Silica Aerogel/GAC composites would provide a water purification technology that meets the needs of Future Combat Systems.

VX: One of the Most Potent Nerve Agents

Nerve agents are the most toxic and rapidly acting of the known chemical warfare agents. VX (O-ethyl-S-2-isopropylaminoethyl-methylphosphonothiolate) is a man-made chemical warfare agent that is the most potent of all nerve agents. In addition, military standards for removal of VX from drinking water are extremely stringent. As a result of these two factors, VX was selected as the appropriate nerve agent to challenge the Silica Aerogel/GAC Composite.

Granular Activated Carbon (GAC) : The Standard for Removal of VX

Previous studies demonstrated that coagulation and filtration alone did not effectively remove VX and other nerve agents from water. Early research demonstrated that removal of chemical agents required super-chlorinating with calcium hypochlorite followed by treatment with activated carbon.^{1,2,3} The activated carbon catalyzes oxidation of VX, removes chlorine, and adsorbs the agent.⁴ As a result, columns of granular activated-carbon (GAC) are incorporated as a post-treatment to remove any VX or other chemical agents that may be present

¹ Larson, R. E., R. J. Petersen, and P. K. Eriksson, Test Results on FT-30 Eight-Inch-Diameter Seawater and Brackish Water Reverse Osmosis Elements, Desalination 46 , 81-90 (1983).

² Lindsten, D. C., and P. R. DesRoches, Decontamination of Water Containing Chemical and Radiological Warfare Agents by Reverse Osmosis, Report 2211, U.S.Army Mobility Equipment Research and Development Command, Fort Belvoir, VA, AD A046203 (1977).

³ Lindsten, Don, Journal AWWA, February 1978, 90-92.

⁴ Khordagui, Hosny, Environment International, 21(4), 1995, pp 363-379.

in the water.⁵ Previous work has evaluated the performance of a variety of different activated carbons to remove nerve agents from water.⁶ While GAC has become the standard for removal of chemical agents, other studies indicated a major disadvantage of GAC was its slow adsorption kinetics⁷.

Silica Aerogels: Nano-engineered for Large Surface Area and Chemical Functionality

The two keys to effective adsorption using reactive media are: (1) a large surface area, and (2) chemical functionalization. A larger surface area increases the number of locations or “sites” to which contaminants may attach or be chemically transformed. Typical activated carbons have surface areas ranging from 600 to 1,200 m²/g. One of the disadvantages of GAC is that there is limited capability to functionalize the material to improve its adsorption. The ideal reactive material would be comprised of the high surface area and large pore volume of GAC with the additional benefit of engineered chemical functionality that would target specific compounds.

Silica aerogels are open foam type materials that have high surface area (>500 m²/g), high porosity (90+%), and low densities (<0.3 g/ml). A transmission electron micrograph of a silica aerogel is shown in Figure 1. These properties lead to enhanced accessibility to adsorption/reaction sites. With the proper synthetic manipulations, the aerogels can be chemically modified to target specific contaminants, such as Uranium or VOCs, or specific properties, such as hydrophobicity⁸. This has led to the use of aerogels in many environmental applications, such as oil-spill cleanup^{9,10}, organic adsorption¹¹, oxidation catalysis¹², and NOx abatement^{13,14}.

Aerogels can be fabricated as a substrate surface coating. With a thin film of aerogel adhering to the surface of GAC media, a synergistic hybrid is created which enables increased adsorption capacity and selectivity. Ongoing research at LLNL by Coleman and others has suggested that GAC surface coated with aerogels increases its ability (four or more times) to remove various contaminants such as uranium, chromium and arsenic, from water supplies¹⁵.

Silica aerogels cannot only be used in standard columns, but can also be impregnated onto various carbonized materials, such as cotton wool (see Figures 2A and 2B). This suggests that silica aerogels may be used to enhance existing separation media technologies. The

⁵ Daniels, I.J.; G.M. Gallegos, Evaluation of Military Field Water Quality, UCRL 21008, May 1990

⁶ Singh, B.; Madhusudhanan, S.; Dubey, V.; Nath, Rabinder, and RAO N.B.S.N., *Carbon*, 34, 1996 327-330

⁷ Mangun, C.; Zhongren, Y.; Economy, J.; Maloney, S.; Kemme, P., Cropek, D., *Chem. Materials*, 2001, 13, 2356-2360.

⁸ Coleman, Sabre J., Paul R. Coronado, and John G. Reynolds, Maxwell, Robert S., Granular Activated Carbon Modified with Hydrophobic Silica Aerogel-Potential Composite Materials for the Removal of Uranium from Aqueous Solutions, *Environ. Sci., Technol.*; 2003; 37(10) pp 2286-2290

⁹ REYNOLDS, J.G.; CORONADO, P. R.; HRUBESH, L.W. *Energy Sources* 2001, 23, 831-843

¹⁰ REYNOLDS, J.G.; CORONADO, P. R.; HRUBESH, L.W. *J. NON-CRYST. SOLIDS*, 2001, 292, 127-137

¹¹ REYNOLDS, J.G.; CORONADO, P. R.; HRUBESH, L.W. *J. NON-CRYST. SOLIDS*, 2001, 285, (1-3), 328-332

¹² HAIR, L. M.; CORONADO, P.R.; REYNOLDS, J.G., *J. NON-CRYST. SOLIDS*, 2000, 270 (1-3), 115-122

¹³ NELSON, A. J.; REYNOLDS, J.G.; SANNER, R.D.; CORONADO, P.R.; HAIR, L.M. *J.VACUUM SCI. TECHNOL. A* 2001, 19(4), 1121-1125

¹⁴ Reynolds, J.G.; Hair, L. M.; Coronado, P.R.; Droegge, M.W.; Wong, J. *Proc., Matter. Res. Soc.* 1997, 454, 225-232

¹⁵ Coleman, Sabre J., Paul R. Coronado, and John G. Reynolds, Removal of Uranium from Groundwater using Granular Activated Carbon Modified with Hydrophobic Silica Aerogel, American Chemical Society Meeting, Orlando, FL 2004.

performance and design flexibility of the silica aerogel materials indicate that these materials could aid in the design of water treatment systems that are more lightweight and exhibit smaller physical footprints than existing systems.

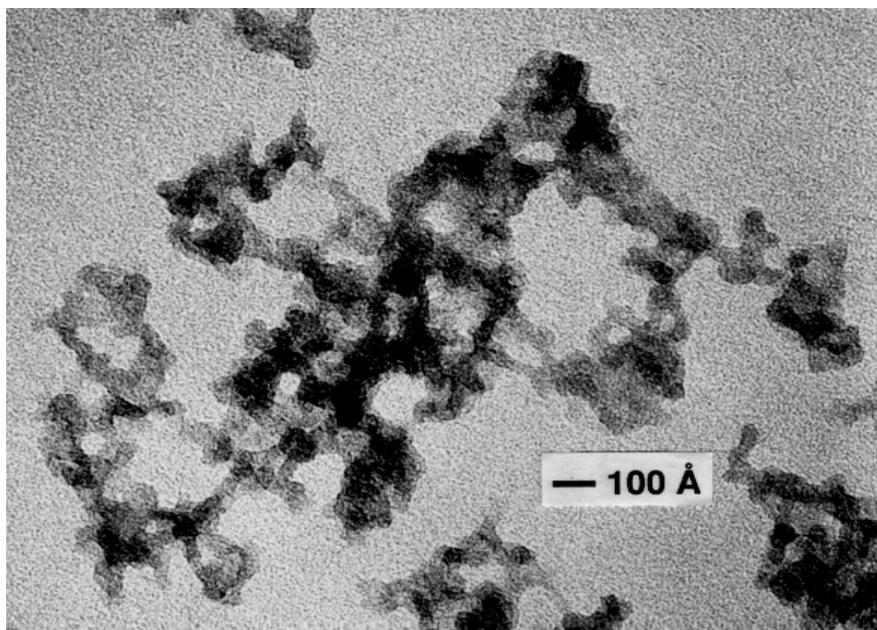
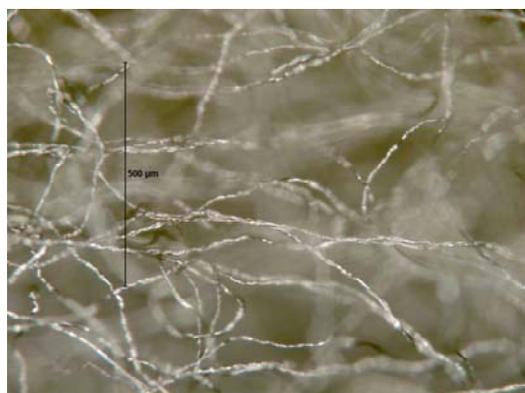
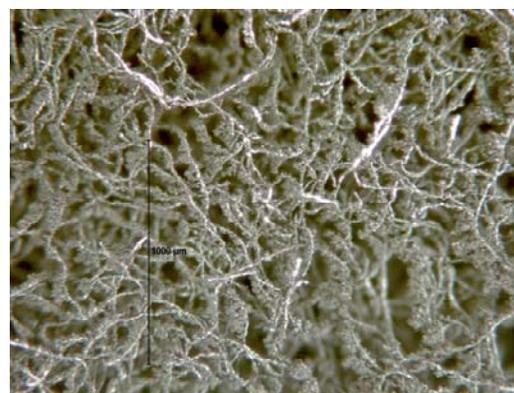


Figure 1. Transmission Electron Micrograph of Silica Aerogel.



A



B

Figure 2. A: Carbonized cotton wool. B: Carbonized wool surface treated with silica aerogel.

Silica Aerogel Materials Adsorbs nearly 30 Times More VX Than GAC

Silica aerogel was manufactured and functionalized to induce hydrophobicity through the incorporation of propyl-CF₃ groups¹⁵. The material exhibited a surface area of 1020 m²/gm and an average pore diameter of 7.38 nm.

Six 20 ml vials were filled with adsorbent ranging from approximately 5 to 110 mg of either silica aerogel or commercially prepared virgin coconut GAC as the adsorbent. The sorbents were exposed to two different solutions containing VX agent at a concentration of

approximately 2 ppm and VX agent at a concentration of approximately 15 ppm. The vials were set on a shaker table and the adsorption allowed to reach equilibrium over a period of 5 minutes. The VX solution in each vial was then sampled and analyzed using liquid chromatography/mass spectrometry (LC/MS).

Figures 3 and 4 compare the ability of the silica aerogel material to adsorb VX from solution to the ability of GAC to adsorb VX from solution. The ratio of concentration of VX in solution to initial concentration of VX in solution is plotted against the mass of adsorbent. In Figure 3, the initial concentration of the VX was approximately 15 ppm. This value was selected based on values used in previous studies of nerve agents in the field^{1,2,3}. The ratio of concentration in solution to initial concentration decreases in value as VX is removed from the solution by the adsorbent. Figure 3 demonstrates that the Silica aerogel is significantly more adsorbent than GAC. When 110 mg of adsorbent was used, the *silica aerogel was nearly 30 times more adsorbent than GAC*.

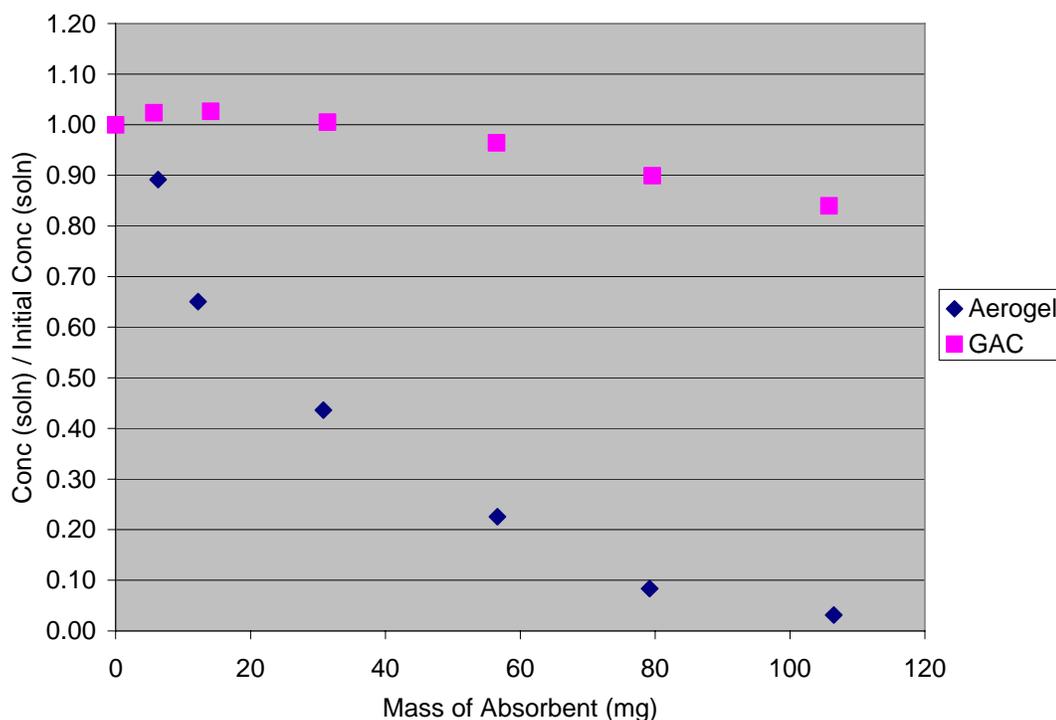


Figure 3. Plot of ratio of concentration of VX in solution to initial concentration of VX in solution vs. mass of adsorbent. Silica aerogel is significantly more adsorbent than GAC, e.g. for 110 mg mass, silica aerogel is nearly 30 times more adsorbent than GAC.

The same approach described above was repeated, except that the initial VX concentration was approximately 2 ppm. The results shown in Figure 4 demonstrate again that for a given weight of adsorbent, the silica aerogel was able to adsorb VX more efficiently from solution than the GAC. In fact, no VX was detected in solution (detection limit ~ 0.05 ppm) when a mass of silica aerogel in excess of 75 mg was used.

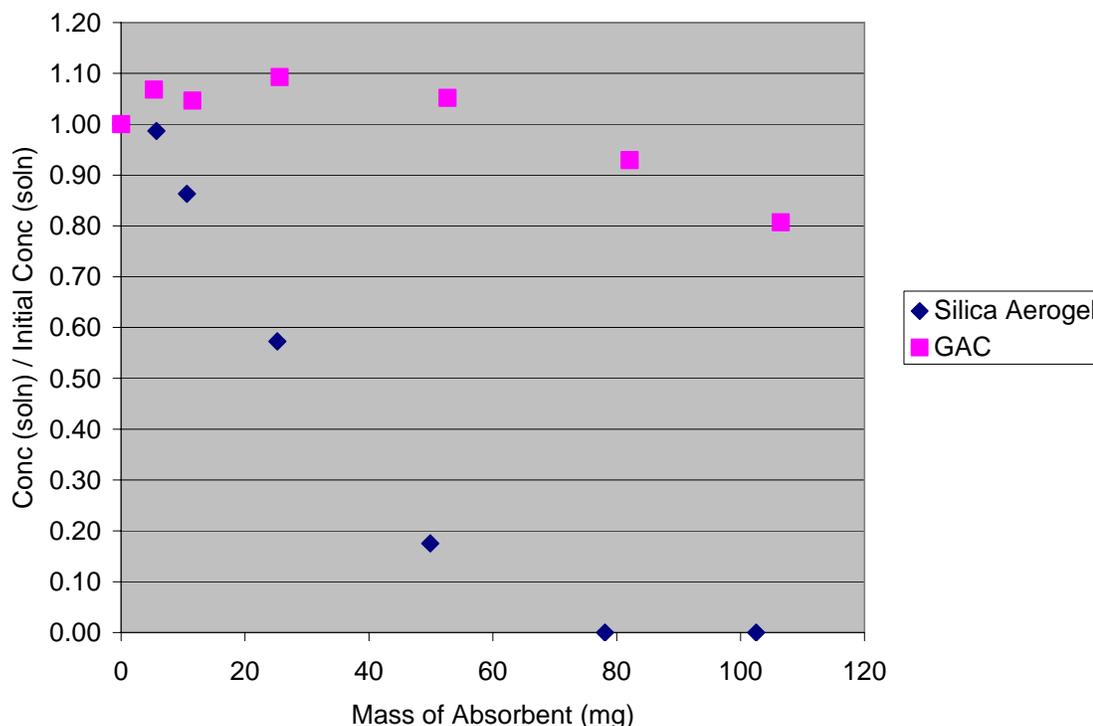


Figure 4. Plot of ratio of concentration of VX in solution vs. mass of adsorbent. Initial concentration of VX solution was approximately 2.5 ppm. No VX was detected in solution when the mass of silica aerogel used was greater than 75 mg.

Silica Aerogel Performance Can Reduce Logistic Footprint and Replenishment Demands

The improved sorptive capability of the silica aerogel can have significant impact on the logistics chain. Consider a treatment system flowing at 50 gpm with 15 ppm of VX in the feed stream. If the system required 200 lb of reactive media, the changeout frequency would decrease from approximately 30 times per year for GAC to approximately once per year for silica aerogel¹⁶. On the other hand, if the replacement frequency were held as the constant then the volume of adsorbent required would be reduced by a factor of 30 (from 200 lb to 7 lb).

Another option is to fabricate a nano-engineered composite that combines silica aerogel with GAC. Silica aerogel/GAC composites have been fabricated previously and are able to combine the desired properties of both the aerogel and GAC. An advantage to a composite is that its physical characteristics are similar to GAC; thus the treatment infrastructure for GAC is an option for its deployment.

Summary

¹⁶ Assuming: VX levels of 15 ppm in feedstream, 200 lbs of reactive media, capacity factor of 0.5 lb (GAC) /lb (contaminant) and 15 lb (silica aerogel)/lb (contaminant).

Silica aerogels have been shown to outperform GAC in their ability to adsorb VX. These materials could have a significant impact in reducing logistics footprints and replenishment demands.